GEORGIA INSTITUTE OF TECHNOLOGY — OFFICE OF CONTRACT ADMINISTRATION

PROJECT ADMINISTRATION DATA SHEET

[x] ORIGINAL [ ] REVISION NO. _____

Project No. A-3432 GTRI/~~GIT~~ DATE 2/9/83

Project Director: ~~J. D. Walton~~ DR. T. L. STARR ~~School~~/Lab EMSL

Sponsor: Office of Naval Research

Type Agreement: Contract No. N00014-83-K-0159

Award Period: From 11/30/82 To 11/29/83 (Performance) 1/31/84 (Reports)

Sponsor Amount: Total Estimated: $ 62,987 Funded: $ 62,987

Cost Sharing Amount: $ None Cost Sharing No: _____

Title: Program To Improve The Strength and Toughness of Sintered Fused Silica

ADMINISTRATIVE DATA OCA Contact Frank H. Huff

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Defense Priority Rating: _____ Military Security Classification: Unclassified

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RESTRICTIONS

See Attached Gov't Supplemental Information Sheet for Additional Requirements.

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Equipment: Title vests with none proposed

COMMENTS:

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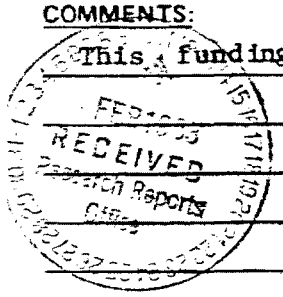

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SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date February 29, 1984

Project No. A-3432 ~~School~~/Lab EMSL

Includes Subproject No.(s) _____

Project Director(s) Tom Starr GTRI / ~~GIT~~

Sponsor Office of Naval Research

Title Program to Improve the Strength and Toughness of Sintered Fused Silica

Effective Completion Date: 11/29/83 (Performance) 1/31/84 (Reports)

Grant/Contract Closeout Actions Remaining:

- [ ] None
- [x] Final Invoice or Final Fiscal Report
- [x] Closing Documents
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A-3432

ENGINEERING EXPERIMENT STATION
Georgia Institute of Technology
A Unit of the University System of Georgia
Atlanta, Georgia 30332

November 11, 1983

Leader, Materials Division
Office of Naval Research
Department of the Navy
Arlington, Virginia 22217

Dear Sir:

The following constitutes the required "End-of-the-Fiscal-Year" letter report for our ONR contract.

1. Title: A Program to Improve the Strength and Toughness of Sintered Fused Silica
   Contract number: N00014-84-K-0159
   Work unit number: NR 651-018
   ONR Scientific Officer: Dr. Robert Pohanka
   Principal Investigator: Mr. Jesse D. Walton (original)
   Dr. Thomas L. Starr (current)

2. Technical results: The ultimate goal of this program is to improve the strength and toughness of sintered fused silica through increased densification and/or fiber reinforcement. This requires development of a silica matrix material that resists divitrification, consolidates to high green density, and can be processed with fibers for composite fabrication. We have screened a number of non-traditional silica materials for sinterability, devitrification resistance, and processing behavior.

   The most promising material results from hydrolysis of ethylsilicate. Under various conditions, this can produce ultrapure silica as a coarse powder (1-40μm) with irregular particle shape, as a fine powder (0.5μm) with a spherical particle shape, or as an organosilican resin with a high silica content. Singly and in combination these materials have demonstrated good sintering and divitrification behavior. Combinations of the powders yield higher green densities than with either alone, due to improved particle packing. The resin can be used as a binder for pressing and molding processes, contributing additional silica to the matrix upon firing.

   Preliminary experiments with ceramic fibers have demonstrated good processing behavior. Ethanol slurries of these matrix materials wet and penetrate bundles of continuous fiber well. Chopped fibers disperse well with no indication of clumping. The fracture surface of fired composites shows a dense, continuous, glassy matrix surrounding the

fibers with apparent debonding at the fiber-matrix interface.

3. Technological significance: Successful development of a strong and tough silica composite will provide a radome material for advanced Navy weapons with maximum mission capabilities under all weather conditions. Our work suggests that such a material can be produced using cold forming and sintering processes. Extension of these techniques to other ceramics will advance high temperature heat engine and energy conversion technology.

4. Presentations. None.

5. Other research. Other major research tasks for the current principal investigator include: "Development of advanced fiber reinforced ceramics" with the DOE Fossil Energy Materials Program ($340K) and "Improved reliability of high-performance coatings" with the FHWA ($282K).

6. Honors or awards. None.

7. Participants. Research faculty participants include Thomas L. Starr, Jesse D. Walton and Joe N. Harris. No post-docs or students participated during this period.

Respectively submitted,

Thomas L. Starr
Energy and Materials Sciences Laboratory

FINAL REPORT

PROGRAM TO IMPROVE THE STRENGTH AND TOUGHNESS OF SINTERED FUSED SILICA

By

T. L. Starr and J. D. Walton, Jr.

Prepared for

OFFICE OF NAVAL RESEARCH
800 NORTH QUINCY STREET
ARLINGTON, VIRGINIA 22217

Under

Contract N00014-83-K-0159

Report for Period 30 November 1982 – 29 November 1983

JANUARY 1984

GEORGIA INSTITUTE OF TECHNOLOGY
A Unit of the University System of Georgia
Engineering Experiment Station
Atlanta, Georgia 30332

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18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Fused Silica
Composites
Brittle Matrix Materials
Materials Processing

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The ultimate objective of this program is to achieve substantial improvement in the mechanical properties of sintered fused silica by increasing the density to which these materials can be processed and by the incorporation of fibers as a second phase into the silica matrix. In the first phase of this research effort high purity fused silica materials were produced from a silica polymer: as a resin, fine powder (0.5-1.0 μm), and coarse powder (1-40μm). These materials exhibited a reduced rate of devitrification compared to high purity slip-cast fused silica. Candidate fibers for incorporation in a silica matrix were

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20. Abstract (continued)

identified and their interaction and packing with matrix powders were explored.

Final Report

Contract N00014-83-K-0159

PROGRAM TO IMPROVE THE STRENGTH AND TOUGHNESS OF SINTERED FUSED SILICA

T. L. Starr and J. D. Walton, Jr.
Georgia Institute of Technology
Engineering Experiment Station
Atlanta, Georgia 30332

January 1984

Report for Period 30 November 1982 - 29 November 1983

Prepared for

Office of Naval Research
800 North Quincy Street
Arlington, VA 22217

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PROGRAM TO IMPROVE THE STRENGTH AND TOUGHNESS OF SINTERED FUSED SILICA

I. INTRODUCTION

Georgia Tech pioneered the development of slip-cast fused silica for radome applications and during the past 10 years led efforts to establish specifications for a standard "high purity" slip. The properties of slip-cast fused silica developed through these efforts have become standardized and were determined basically by the purity of the raw material and the ball milling, slip-casting and sintering processes.

For current hypersonic applications the strength and rain erosion properties of the standard, high purity slip-cast fused silica are adequate, but future mission capabilities will have to be compromised unless these properties can be significantly improved. Two modifications to the basic material/process offer promise for providing the required improvement: (1) increasing the density of the sintered product, and (2) incorporating a second phase into the fused silica matrix.

The present high purity slip-cast fused silica (radome material) is sintered to a density of 1.95 to 1.96 gm/cm^3 (88-89 percent dense). This density has been optimized based on the strength of the sintered product which is determined by the amount of cristobalite which is formed during the sintering process. The porosity of the fused silica is predominantly open and therefore requires sealing to prevent moisture absorption. Although the porous structure limits the strength of this material to about 35 MPa (5000 psi), it provides a material with some degree of toughness with respect to rain damage resulting in incremental erosion rather than catastrophic failure. Although the rain erosion behavior may be adversely

affected by increasing the density of slip-cast fused silica, it is not clear that the accompanying increase in strength will not offset the change in rain erosion mechanism, at least up to the velocity of threshold damage.

Two methods have been reported for increasing the density of sintered fused silica without the development of excessive cristobalite. One involves the use of ultra-pure particulate fused silica 1/ and the other a silica gel either by sol-gel technology 2/ or from "fumed" colloidal silica 3/. The first method permits the use of conventional fused silica slips facilitating the fabrication of parts from this material. The second method presents serious fabrication problems but may provide a more suitable matrix material in which to incorporate second phase additions.

Ultra pure slip-cast fused silica has been sintered to 98 percent of theoretical density essentially free of cristobalite, but with only a moderate increase in strength, 48 MPa (7000 psi) 1/. However, this material was produced for its optical properties and the particle size distribution and was not chosen for maximum strength.

"Fumed" silica has been used to produce transparent, sintered "fused" silica as well as a 97 percent SiO_2 - 3 percent B_2O_3 glass. The silica glass exhibited a strength of 69 MPa (10,000 psi) and the 97 percent SiO_2 glass 130 MPa (19,000 psi) 3/.

In addition to the purity of the raw material the firing atmosphere also can influence the development of cristobalite as can impurities in the slip or other contamination of the surface of the fused silica particles 4/. Water vapor and oxygen in the furnace atmosphere have been shown to accelerate devitrification while vacuum sintering or sintering in H_2O and O_2 free nitrogen, helium and argon have been found to reduce the rate of cristobalite formation 5/.

At the present time it is not clear just how pure the raw material must be in order to achieve the density/strength improvement needed for advanced radome applications. It is clear, however, that all contaminants which contribute to the devitrification must be eliminated (in the slip, on the particle surfaces and in the furnace atmosphere). Ideally, removing these contaminants from the currently used slip would be the most desirable approach since fabrication methods have been established using this material. Work at GE suggests that the devitrification rate of the raw material used in the present high purity fused silica slip (GE-204) can be substantially reduced by properly cleaning the surface and firing in an atmosphere free of O_2 and H_2O 4/.

The thermophysical properties of fused silica make it a promising matrix material for strengthening with second phase additions. Such additions would be expected to play a critical role in compensating for any loss in toughness which may result from the increased density proposed in the previous section. At the same time, in order to effect substantial strengthening from second phase addition, particularly fibers, it is important that a maximum interfacial contact area be developed between the matrix and the fiber, and that the matrix material be as free of voids as possible. Therefore in order to develop a high strength fused silica matrix composite it is important that the silica reach as high a density as possible during the sintering operation. It also is important that the physical properties of the fibers not be degraded during sintering.

A number of programs have successfully demonstrated the exceptional properties which can be obtained by reinforcing high density glass matrices with various metal, carbon and oxide fibers. Work at UTRC resulted in the

development of a 37 volume percent aluminum oxide fiber reinforced fused silica matrix with a flexural strength of 160-170 MPa (20,000-25,000 psi) from room temperature to at least 1000° C 6/. However, all of these efforts have involved forming methods using hot pressing techniques, thus limiting their potential for radome fabrication. Future radome fabrication efforts would be greatly facilitated by the development of a fiber reinforced fused silica matrix composite which could be fabricated using a cold forming process followed by sintering in air or an inert atmosphere.

Previous efforts at AMMRC 7/ and Georgia Tech 8/ have demonstrated that 25 to 50 volume percent chopped fibers can be incorporated into existing fused silica slips. Unfortunately, reinforcement by these fibers has been minimal since matrix densities were low and overall composite densities generally decreased as fiber content increased. However, by applying sol-gel technology, and/or developing fused silica slips which can be sintered to near theoretical densities it seems reasonable to expect that high density fused silica matrix composites can be developed with significantly improved strength and toughness and which can be fabricated using more conventional cold forming processes.

As pointed out previously, fused silica is an attractive matrix material with which to develop a broad range of ceramic matrix composites. Those properties which make it attractive are low modulus, low thermal expansion and visco-elastic behavior. Typically it is desirable that the reinforcement have a higher modulus and thermal expansion than the matrix material 9/. This will be the case for essentially all reinforcement materials in a fused silica matrix. Assuming good interfacial bonding, the fiber will be prestressed in tension during cooling from the sintering temperature. For room temperature applications this prestress should

significantly increase the strength and toughness of the silica. At high temperatures the viscous behavior of the silica will provide an alternate load transfer mechanism as the degree of fiber prestress decreases 10/. If these relationships can be demonstrated experimentally, using cold forming techniques, then fiber reinforced silica would have the potential of becoming the high temperature analog of fiber reinforced plastics, not only for radomes but for a wide range of high temperature structural applications as well.

The ultimate objective of this program is to achieve substantial improvement in the mechanical properties of sintered fused silica by increasing the density to which these materials can be processed, with corresponding reduction in porosity, and by the incorporation of second phases, such as fibers, into the silica matrix. Accomplishing this is expected to take several years of investigation. The objective of the initial phase of this program, reported here, is to explore a number of processing and compositional paths to the extent that those having good potential for success can be identified. In this context, good potential for success will be attributed to those paths in which experimental results show that substantial improvements in material properties are probable, using cold-forming fabrication technology and conventional heat treatment methods, including controlled atmosphere sintering but excluding, for example, hot-pressing in dies or isostatically. In the area of sample characterization, variables such as density, crystalline phases, and microstructure will be emphasized initially, since these reveal the degree of success toward meeting the program objectives with limited quantities of sample materials and simple measurement procedures.

II. IMPROVED SILICA MATERIALS

We obtained or produced several non-conventional silica materials which we expected to exhibit improved sintering behavior and resistance to devitrification. These include milled ultra pure fused silica and high silica glasses, and synthetic silica powders and resins.

Ultra Pure Fused Silica and High-Silica Glasses

We prepared casting slips from four types of fused silica and high silica glasses: (1) Spectrosil® - an ultra high purity fused silica containing less than 1 ppm total impurities, (2) conventional "high purity" fused silica, less than 0.5 percent impurities, (3) Vycor®, a 96 percent SiO_2 glass containing about 4 percent B_2O_3, and (4) Pyrex®, a borosilicate glass containing approximately 80 percent SiO_2. We included Vycor® and Pyrex® in this study because of the extensive use of these materials in other ceramic fiber reinforced glass matrix composite work using hot pressing techniques. Thus, it they could be cold formed and sintered to high density we would have a potential matrix material available for reinforcement and comparison with hot pressed composites.

Except for the commercial "high purity" fused silica, initial slips were prepared by wet grinding 500 gm of 4 to 8 mesh cullet with 175 gm of distilled water in a one gallon high purity alumina ball mill. About 5-1/2 kg of 19 mm diameter high density alumina spheres were used as the grinding medium. Each slip was prepared by milling at 45 rpm (about 60 percent of critical speed) for 24 hours. Water was adjusted during milling to achieve a castable slip viscosity with the resulting slips ranging from 73 to 80 percent solids. The high purity fused silica was obtained either as a commercially prepared slip or as a commercial spray dried powder which was reconstituted to form a slip by adding water. Each slip was used to

slip-cast solid bars 19 mm in diameter and 175 mm long. These bars were used for sintering and devitrification studies.

In addition to the fused silica and high silica glasses we prepared slips and powders from amorphous, calcined silica materials prepared from ethyl silicate (described in the next section). In order to minimize inorganic contamination from the ball mill we constructed a small polycarbonate ball mill (about 1.3 liters). About 900 gm of grinding media was used which consisted of cylinders with an L/D of 1 cut from 9 and 13 mm diameter Spectrosil® rods.

Synthetic Silica

Very high purity silica can be produced by chemical conversion of non-oxide silicon compounds. The degree of purity depends on the purity of the starting materials and the care in handling during production and storage of the material. Such silica materials can be produced in a wider range of physical states than is possible with milled materials.

A synthetic silica material, commercially available as Cab-O-Sil,® is produced by the hydrolysis of silicon tetrachloride vapor in a flame of hydrogen and oxygen, as shown in the reactions:

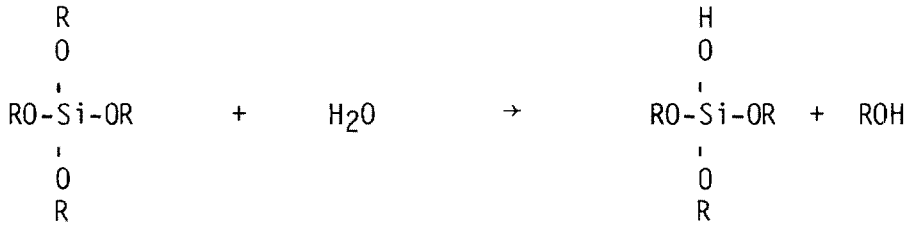
$$2\ H_2 + O_2 \rightarrow 2\ H_2O$$

$$n\ SiCl_4 + 2n\ H_2O \rightarrow (SiO_2)_n + 4n\ HCl$$

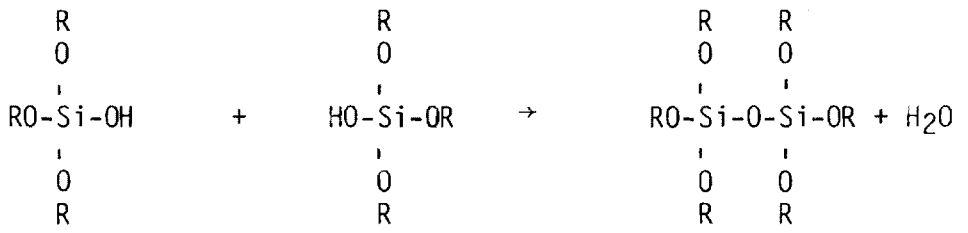
This "fumed" silica consists of branched, chain-like aggregates of silica spheres. The spheres, ranging in diameter from 0.007 to 0.14 μm are fused together in the chains and cannot be separated into individual particles using normal grinding methods 11/. While densification of this material has been reported 3/, the powder has a very low bulk density (0.03 - 0.06 g/cc) which results in a great deal of shrinkage during sintering.

Other high purity silica materials can be produced by hydrolysis of ethyl silicate in solution under acid or alkaline conditions. The overall reaction consists of a hydrolysis step and a condensation step:

Hydrolysis



Condensation



Continued hydrolysis and condensation result in formation of a complex silica network. In theory, complete reaction requires two moles of water per mole of ethyl silicate.

$$n\ Si(OR)_4 + 2n\ H_2O \rightarrow (SiO_2)_n + 4n\ R\text{-}OH$$

In practice, this reaction does not proceed to completion but forms a condensation product with residual hydroxyl and, in some cases, residual ethoxy groups appended to the network. The final reaction product depends on the reaction conditions (amount of water, pH, concentration of reactants) and can vary from a resin-like polymer to a hard gel to a suspension of colloidal silica 12,13/.

We prepared a coarse silica powder, similar in particle shape and size distribution to standard silica powder, by milling of a hydrolyzed ethyl silicate gel. The gel was prepared in ethanol by addition of water and acid as shown in Table 1. This reaction proceeds rapidly, as evidenced by spontaneous heating of the solution, and forms a soft gel, completely filling the vessel, overnight. This gel was removed from the vessel, dried at 105° for several hours, calcined at 450° C and ground in a polycarbonate ball mill using fused silica grinding media. Polycarbonate contamination was removed by a second calcining after grinding. Figures 1 and 2 show the particle shape and size distribution of this powder, consisting of angular particles in the range of 1-40 μm.

TABLE 1

SILICA MATERIALS FROM ETHYL SILICATE

	Gel	Spheres	Resin
Solvent	Ethanol	Ethanol	Ethanol
Con. TEOS (g/ml)	0.35	0.09	0.35
Moles H_2O/Moles TEOS	10	10	2
Acid/Base	0.006 N HCl	1.4 N NH_3	0.006 N HCl

We prepared a fine silica powder consisting of fine spherical particles by hydrolysis of ethyl silicate under alkaline conditions 11/ as shown in Table 1. The reaction was rapid resulting in a suspension of fine particles in less than ten minutes after ethyl silicate addition. Further treatment to produce a dry powder varied. In some cases we simply

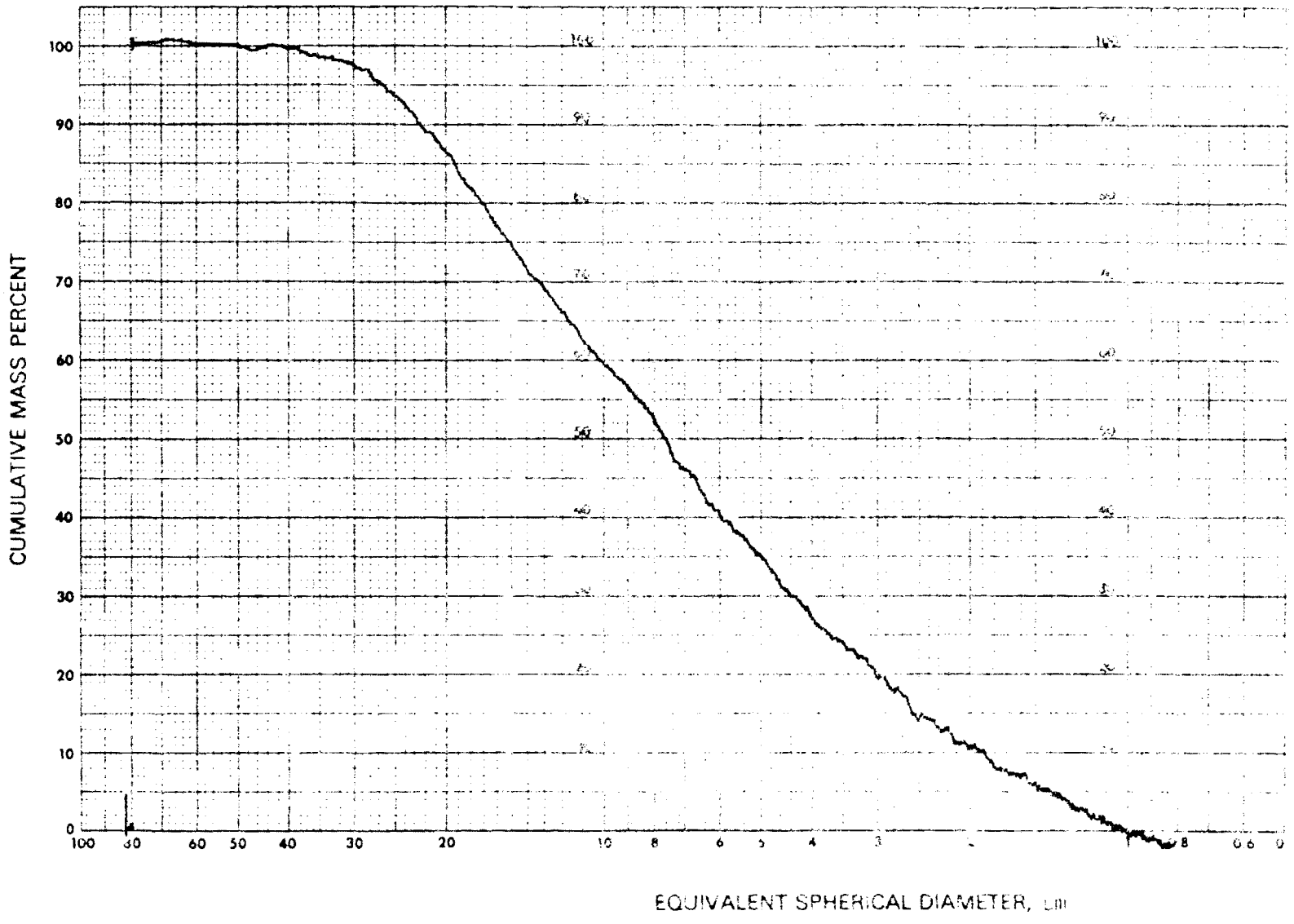


Figure 1. Particle Size Distribution of Coarse Powder.

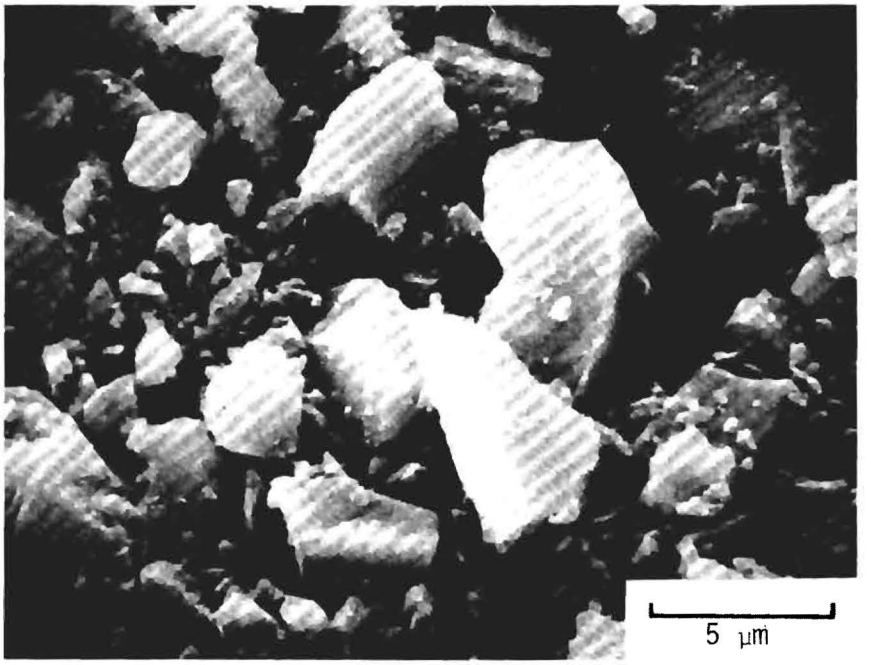


Figure 2. SEM Micrograph of Coarse Powder from Ethyl Silicate.

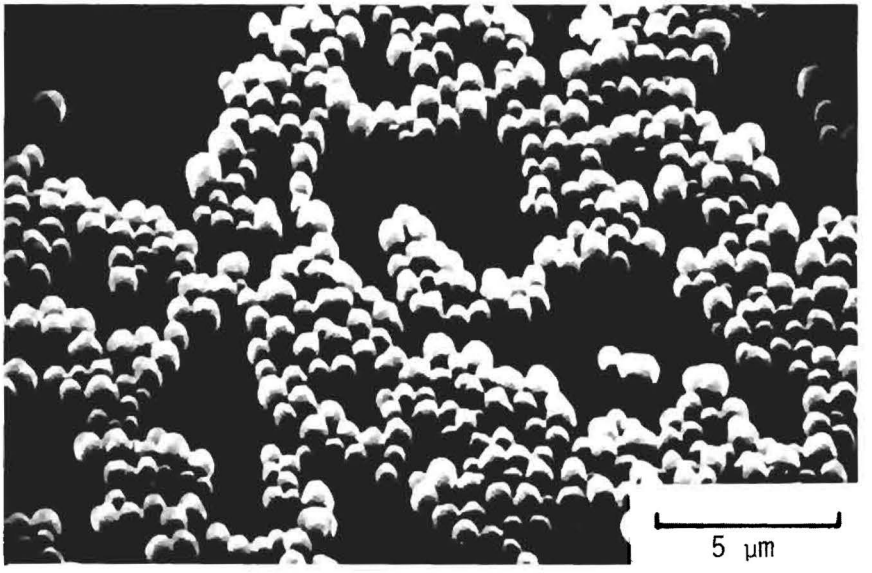


Figure 3. SEM Micrograph of Fine Powder from Ethyl Silicate.

evaporated the liquid leaving the dried powder. In other cases we centrifuged the suspension and decanted the liquid. Further, of the centrifuged materials, some were acid washed to neutralize the residual ammonia. The final step in each method consisted of drying the powder at 110° C. The powder consists of spherical particles with a uniform particle size near 0.5 μm, as seen in Figure 3.

We prepared a high silica resin by acid hydrolysis of TEOS with the stoichiometric amount of water, as shown in Table 1. This resin solution, containing 0.1 g equivalent SiO_2/cc, does not gel even after several months storage. Evaporation of the solvent yields a viscous, pourable fluid containing 0.7 g SiO_2/cc. This concentrate is not stable but reacts with atmospheric moisture over a period of time forming a brittle solid.

The 2:1 mole ratio of water to ethyl silicate appears to yield the highest possible silica density 12/. Hydrolysis with less water (such as commercially important Ethyl Silicate 40 with a mole ratio near 1:1) yields a resin with a silica density of approximately 0.4 g/cc. Hydrolysis with more water results in formation of a porous gel with a specific volume that increases with the amount of water, resulting in a decrease in the silica density.

The three hydrolysis products of ethyl silicate described above offer potential for a variety of processing techniques for silica articles and composites.

III. DEVITRIFICATION AND SINTERING BEHAVIOR OF SILICA MATRIX MATERIALS

Experimental Design

A small, controlled atmosphere tube furnace was constructed for use in studying the devitrification and sintering behavior of experimental compositions. Using silicon carbide heating elements, and a 50 mm ID aluminum oxide tube to contain the desired atmosphere, this furnace was capable of reaching 1500° C and was equipped so that firing could be accomplished in vacuum or at atmopheric pressure in air, argon or helium (see Appendix for detailed description of the furnace).

Rate of heating and temperature control was by manual operation. Firing cycles were carried out which permitted temperature control during normal working hours. The rate of heating was typically the maximum recommended for the aluminum oxide tube, i.e., about 300° C/hr and the firing time reported was the time held at the maximum temperature for any particular firing. Initially aluminum oxide boats were used to support the experimental samples in the tube furnace during firing. Later, in order to minimize the possibility of contamination from the boat, we used broken pieces of thin-wall, transparent fused silica tubes about 50 to 100 mm long and 25 to 40 mm in diameter.

We considered the firing conditions which are known to affect the sintering and devitrification of amorphous silica and identified at least the following:

Rate of heating

Maximum temperature

Time at temperature

Composition and pressure of firing atmosphere.

Since we were evaluating many different sources of silica prepared in different ways and different mixtures of these materials with and without fibers, it was not possible to make an extensive study of the effect of the different firing conditions for each of the compositions and treatments. Thus we decided to concentrate on material preparation and treatment, and to select only a few firing conditions based on our previous experience with silica. Thus the firing temperatures and times were those which should produce substantial densification, and which, using typical slip-cast fused silica should result in significant devitrification.

Ultrapure Fused Silica and High Silica Glasses

Initial sintering experiments were conducted on samples cast from the high purity fused silica slips. We fired two samples at 1450° C for 2 hours, one in air and one in argon. The one fired in argon had been acid washed to remove surface impurities and, thus, to reduce the tendency to devitrify. Both samples were devitrified giving 61-84 percent cristobalite. The slip-cast Spectrosil® was fired at 1500° C for 2 hours in helium and likewise devitrified giving 80 percent cristobalite. From these tests it appeared that the impurity level of the "high purity" silica was too high to benefit from the controlled atmosphere firing. Also it appeared that Spectrosil® was sufficiently contaminated from the milling operation that its natural resistance to devitrification was severely reduced.

We fired the slip-cast Vycor® (96 percent SiO_2) samples at 1480° and 1510° C for 1-1/2 hours and 2 hours in helium. In all cases the Vycor® sintered to 98 percent of theoretical density with little devitrification (0.9 percent cristobalite when fired at 1480° C for 1-1/2 hours). This was

not unexpected since the boron in Vycor® is known to stabilize the amorphous or glassy state of silica 14/.

Slip-cast Pyrex® was fired at 840° and 890° C for 1-1/2 hours in air and vacuum. All samples were glassy in appearance, exhibited a gray color presumably from ball mill contamination, and gave no evidence of devitrification. These samples sintered to a density of 96 percent of theoretical.

Synthetic Silica

The very fluffy, low density nature of Cab-O-Sil silica powder (7 lb/ft^3) required that it be densified in order to prepare samples suitable for sintering and devitrification studies. To accomplish this we added Cab-O-Sil powder to distilled water which was adjusted with ammonia to a pH of about 11. With stirring and with the use of ultrasonic agitation it was possible to obtain an aqueous dispersion containing about 20 weight percent SiO_2. Samples of this dispersion were air dried and fired for 1-1/2 and 2-1/2 hours at 1450° C in helium. From this treatment we obtained a product which was almost completely devitrified, giving 84 percent cristobalite.

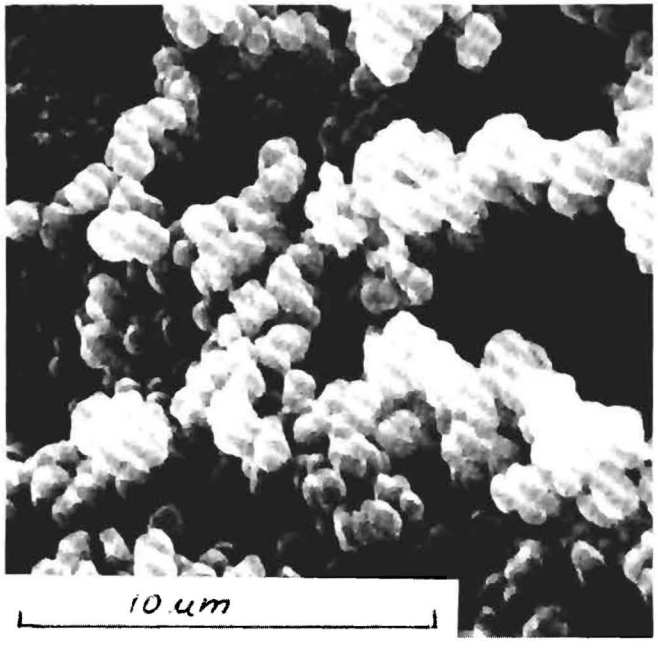
During preparation and sintering of the fine silica powder (spheres) a number of process variables were evaluated. The hydrolysis of ethyl silicate under alkaline conditions was carried out both in glass and plastic containers. The powder was sometimes left to dry in the precursor liquid and sometimes centrifuged and the liquid decanted. The remaining precipitated spheres were sometimes dried, sometimes washed with distilled water, ethyl alcohol, acid or alkali and then dried. The dried spheres were sometimes sintered as dried, loose powders and sometimes pressed

between plastic sheets before sintering. Firing cycles varied from 1200° to 1370° C for 2 or 8 hours in air, vacuum, argon and helium. The results of 29 experimental firings were inconclusive as far as identifying the processing conditions which would consistently provide a sintered high density, transparent or translucent glass. For example, cristobalite contents varied randomly from 0.9 to 80 percent, However, during the course of this study we did conclude that certain steps appeared to improve the resistance to devitrification such as carrying out the reaction in plastic containers and removing the precursor liquid from the precipitated spheres before drying. Also it appeared that the spheres should not be completely dried until near the time they are to be sintered or incorporated into some other composition. Washing with ethyl alcohol, acid or alkali all on occasion gave good results. Relatively high density glasses with less than 1 percent cristobalite were obtained from material either loose or pressed, and fired in either air or vacuum at 1370° C for 2 hours or 1315° C for 8 hours. Figure 4 shows the sintering behavior of this powder.

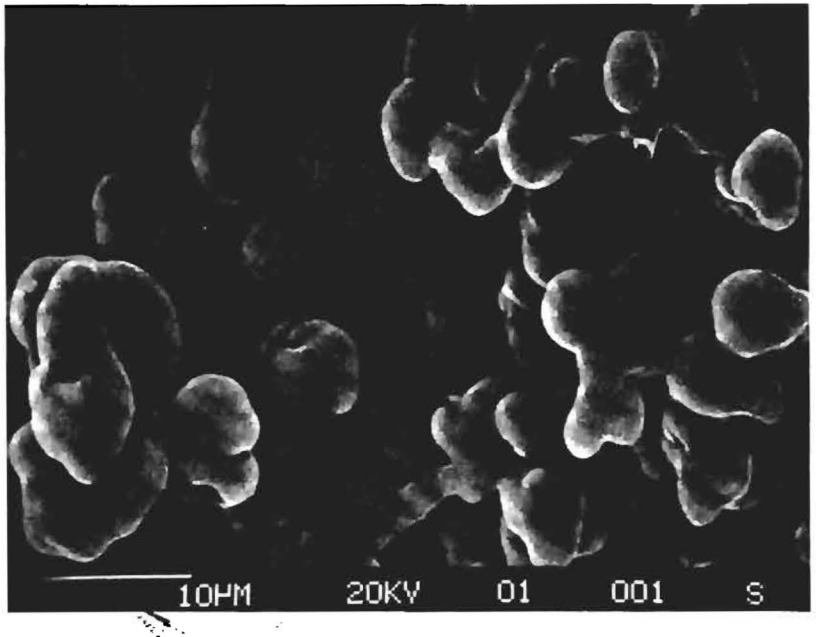
In general we found that the gel, obtained from hydrolyzed ethyl silicate, dried, and calcined at 450° C provided an essentially pure silica material which exhibited the greatest resistance to devitrification. Out of 10 experimental firings, glassy, vitreous products were obtained, fired either in air or vacuum at 1370° C for 2 hours. Cristobalite content was only about 0.5 percent under both conditions. The calcined gel which was ground in the polycarbonate (coarse powder) was not consistently as resistant to devitrification as the unmilled gel. However, we did have one firing of the milled gel at 1370° C for 2 hours in vacuum which produced a translucent glass with only about 0.5 percent cristobalite.

Figure 4. Fine Spherical Powder From Ethyl Silicate
(a) as-settled,
(b) settled and fired,
(c) pressed and fired.

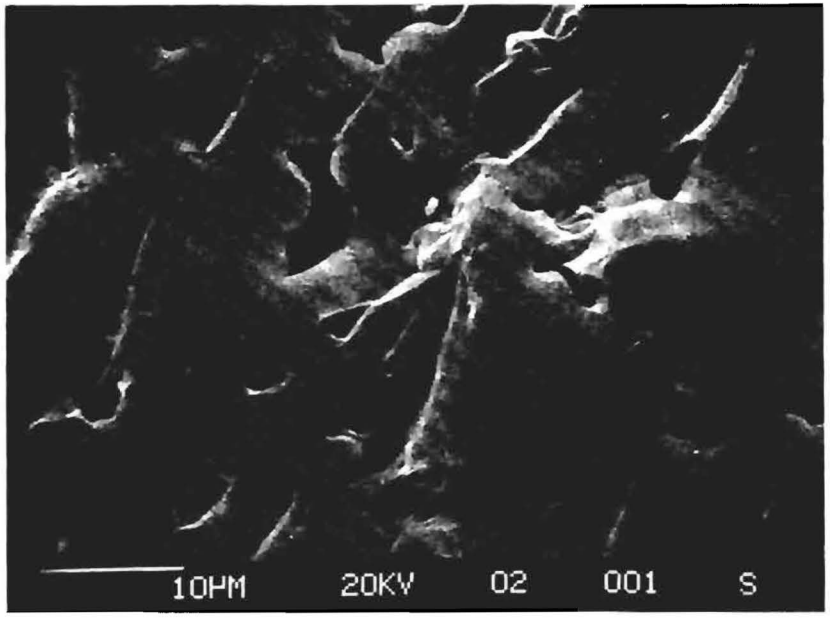
a.



b.



c.



The silica resin was found to act similar to the gel with respect to devitrification. In most sintering studies, however, the resin was used in combination with either the silica spheres or the milled gel or a combination of both. In two cases mixtures of resin and spheres provided an essentially transparent product when fired at 1315° C for 8 hours in vacuum, suggesting that the resin may act to increase the stability of the spheres with respect to devitrification. The cristobalite content of one combination of milled gel, spheres and silica resin was 0.9 percent when fired at 1370° C for 2 hours in vacuum.

Day-to-day variation in devitrification results for materials processed and sintered under supposedly identical conditions indicated that not all of the important process variables were being controlled. It becomes apparent that casual contamination of the materials at various stages of the process was an important factor in devitrification resistance. This was particularly true in the case of the silica spheres made by the hydrolysis of ethyl silicate. We found that for best results the mixture should be centrifuged and the excess liquid removed. Also, the spheres should be kept covered and left in the remaining liquid until time to use. Once the spheres were dried they should be used or kept in a desiccator. Washing with acid, base or ethyl alcohol after centrifuging sometimes appeared to improve sintering, but this could not be confirmed. The dried gel and silica resin appeared to be less sensitive to processing variables but did not always produce a cristobalite free material when fired.

Because of the problems of controlling the conditions of material processing and the interdependency between the character of the material and firing conditions, we have not yet developed an optimum or standard firing cycle. However, best results were obtained when we fired in a vacuum with a small amount of high purity carbon in the hot zone of the furnace between the sample and the vacuum pump to act as a getter.

In summary we have successfully prepared, from ethyl silicate, three different forms of very high purity amorphous silica with the necessary physical characteristics for compounding into high density silica. Figure 5 illustrates the principal steps in each of these processes. Each of these products has been fired to greater than 95 percent of theoretical density with less than one percent cristobalite formation as shown in Table 2.

TABLE 2

SUMMARY OF FIRING STUDIES OF MILLED GEL, SILICA SPHERES AND SILICA RESIN

Material	Firing Cycle	Cristobalite (%)
Milled gel - (coarse powder)	1370° C - 2 hrs-Air	0.5
	1370° C - 2 hrs-Vacuum	0.5
Silica Spheres (fine powder)	1370° C - 2 hrs-Air	0.9
	1315° C - 8 hrs-Vacuum	0.8
Silica Resin	1370° C - 2 hrs-Air	0.5
Mixture of powder, spheres and resin	1370° C - 2 hrs-Vacuum	0.9

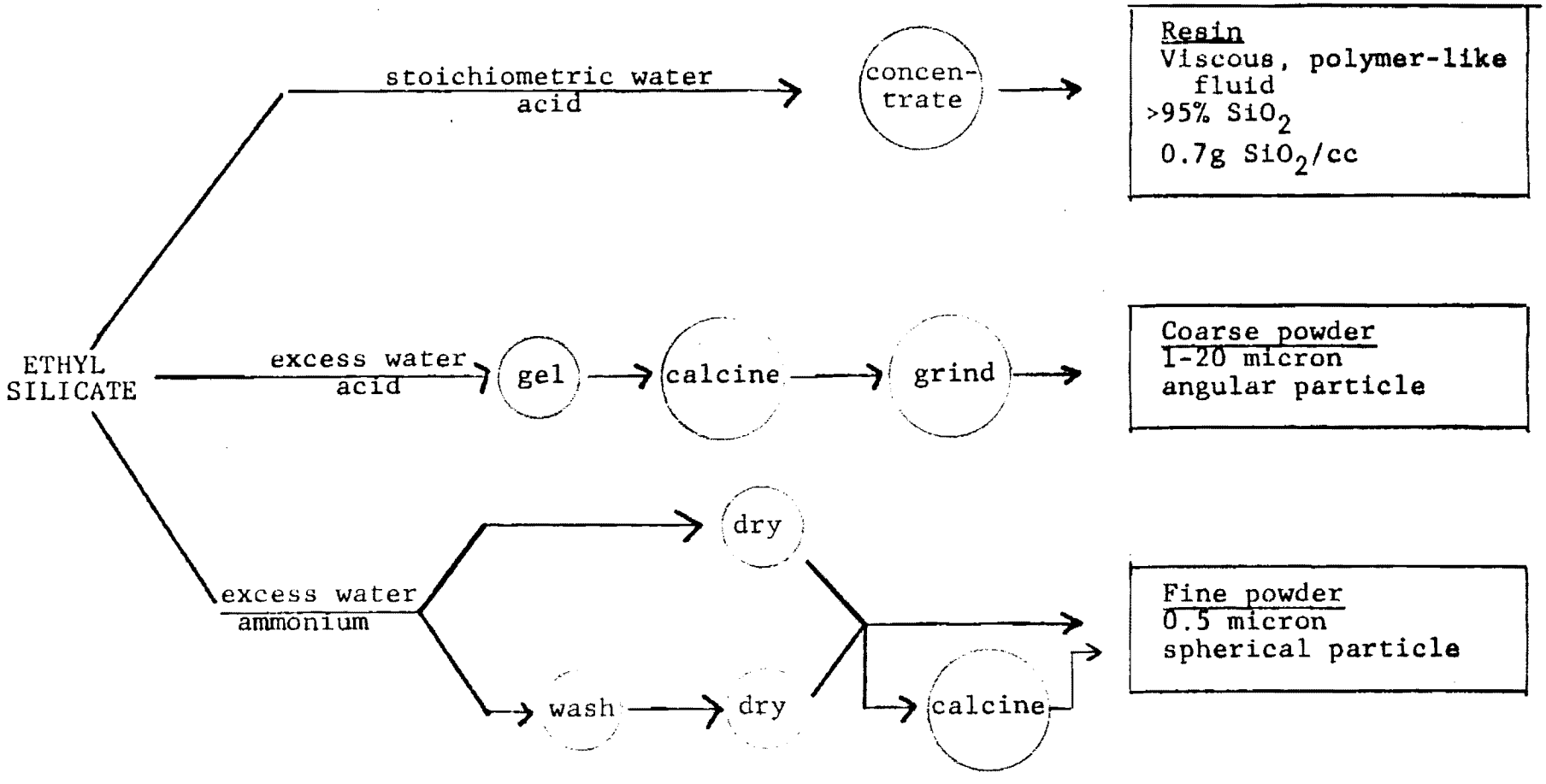


Figure 5. Preparation of Synthetic Silica from Ethyl Silicate.

IV. COMPOSITE PROCESSING

Matrix Green Density

An important requirement for a suitable matrix material is that it be formable to a high green density. A strategy for developing such a material is based on the concept of critical powder volume concentration (CPVC). In mixtures of powder in a continuous phase (resin), there is a unique composition that corresponds to maximum density. At this point, the powder is packed to its greatest density and the resin completely fills the interstitial voids. The density and composition of such mixtures can be calculated knowing the density of the resin, the packing density of the powder, and the density of the individual powder particles. This is shown graphically in Figure 6 for mixtures of the three ethyl silicate based materials described above. The lines rising to the right give the specific volume of resin-rich mixtures, while the lines rising to the left give the specific volume of resin-poor mnixtures. The maximum density (minimum specific volume) is obtained at the intersection of these two lines. The solid lines represent mixtures of the fine, spherical powder and silica resin. The dashed lines represent mixtures of the coarse, angular powder and a continuous phase consisting of the optimum mixture of resin/spheres. For this system, a green density approximately 90 percent of theoretical should be obtainable even though the coarse powder alone only packs to 67 percent. Optimization of particle size distribution to obtain better powder packing could lead to even higher green density.

While such high green densities have not been achieved, as yet, in the experimental program, the validity of this approach has been demonstrated.

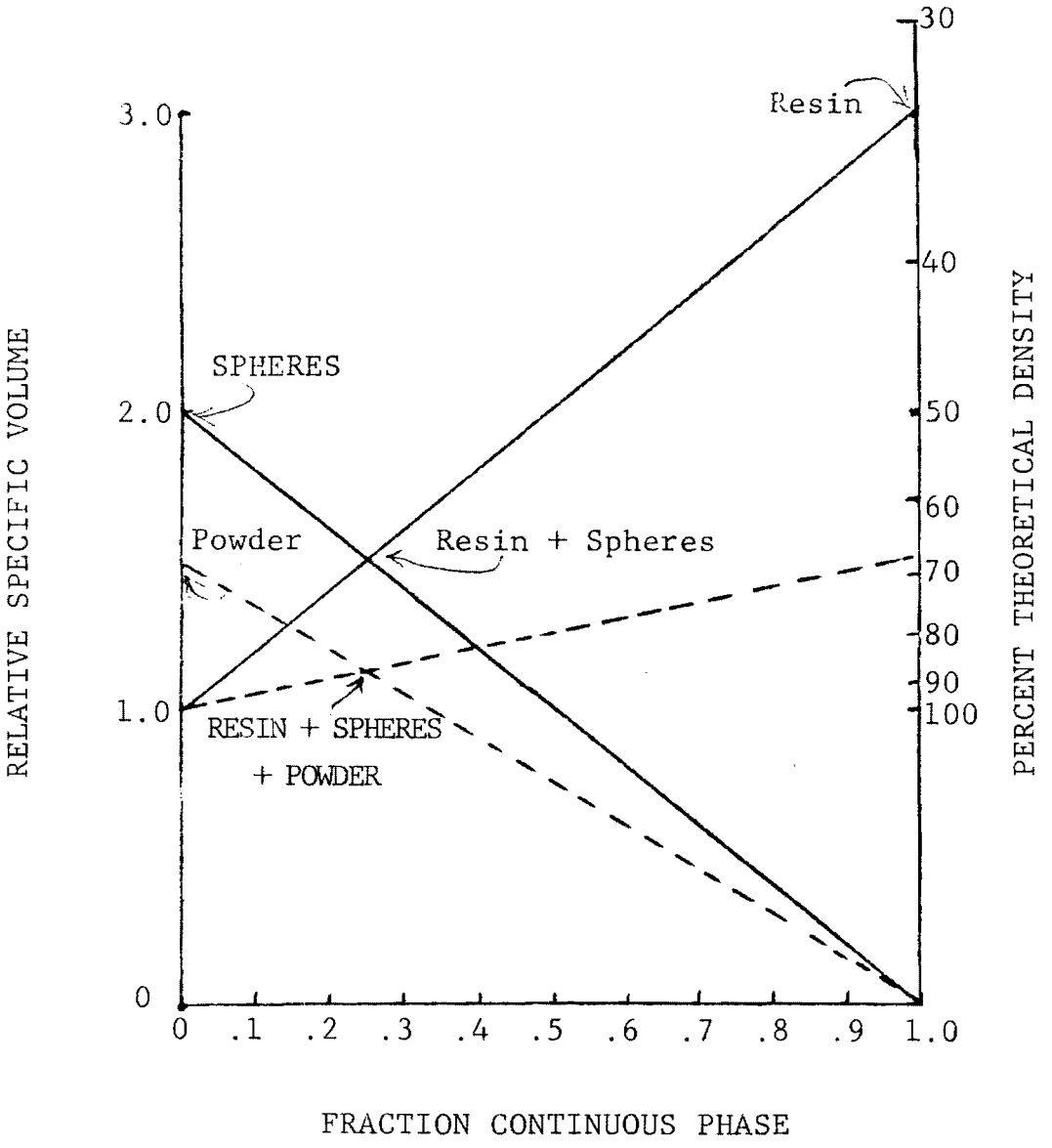


Figure 6. Formulating for Maximum Green Density Resin + Spheres + Powder.

Mixtures of the silica resin and the fine, spherical powder show a maximum green density near the expected resin loading, and a three component mixture at the indicated composition can be pressed and sintered to 98 percent theoretical density.

Fiber Selection and Preparation

Since the primary purpose of this program is to improve the strength and toughness of "fused" (amorphous) silica for advanced radome applications, the choice of reinforcements was necessarily limited to dielectric materials. For this preliminary effort the materials selected were fibers containing Al_2O_3. Both continuous and chopped fibers were considered. DuPont FP was selected for the continuous fiber and 3M Nextel was selected as the chopped fiber. Some properties of these fibers are given in Table 3.

TABLE 3.

HIGH ALUMINA FIBERS

	Nextel	FP
Tensile modulus	152 GPa (22 Mpsi)	350 GPa (50 Mpsi)
Tensile strength	1550 MPa (225 Kpsi)	1380 MPa (200 Kpsi)
Melting point	1700° C (3100° F)	2045° C (3713° F)
Density	2.70 g/cc	3.90 g/cc
Composition	64 $Al_2O_3 \cdot 14B_2O_3 \cdot 24SiO_2$	α-Al_2O_3 (SiO_2 coated)
Diameter	10 μm	20 μm

Initial experiments were carried out with 1/8 inch Nextel fiber 10-12 μm in diameter. In order to obtain a dispersion of fibers suitable for reinforcing the silica matrix, we used a 1-1/4 liter Osterizer blender to disperse and chop the fiber which, when received, had agglomerated into small bundles. To determine the effect of fiber length on packing density the as-received fiber was chopped in the blender using 5 gm of fiber in 250 ml of water for 1-1/4, 2-1/2, 5 and 10 minutes. The fibers were then vacuum filtered in a 1-inch diameter cylinder and the packing density and fiber L/D ratio measured. The results of this experiment are shown in Figure 7. Since the 5 minute chopping time gave a reasonable packing density with an L/D range of 40 to 50, we used this procedure to prepare chopped fibers for use in initial composite fabrication efforts.

Early in this program we prepared composites using chopped fibers dispersed in water and mixed with fused silica slip. The mixture was then dewatered and "felted" to provide the composite sample. Although the distribution of particle sizes in the slip had been adjusted to provide only -5 μm particles to facilitate packing (less than 1/2 the fiber diameter), the green density of the compacts was low and decreased with increasing fiber concentration (10, 20 and 40 volume percent fiber gave 1.6, 1.4 and 1.2 gm/cc fired densities respectively). From these initial results we decided to delay further work with chopped fibers and fused silica slip.

As the work progressed in the development of the promising three component matrix (previously described) we prepared samples of composites using the continuous FP, aluminum oxide fiber. This matrix had the potential of achieving higher green and fired densities than the

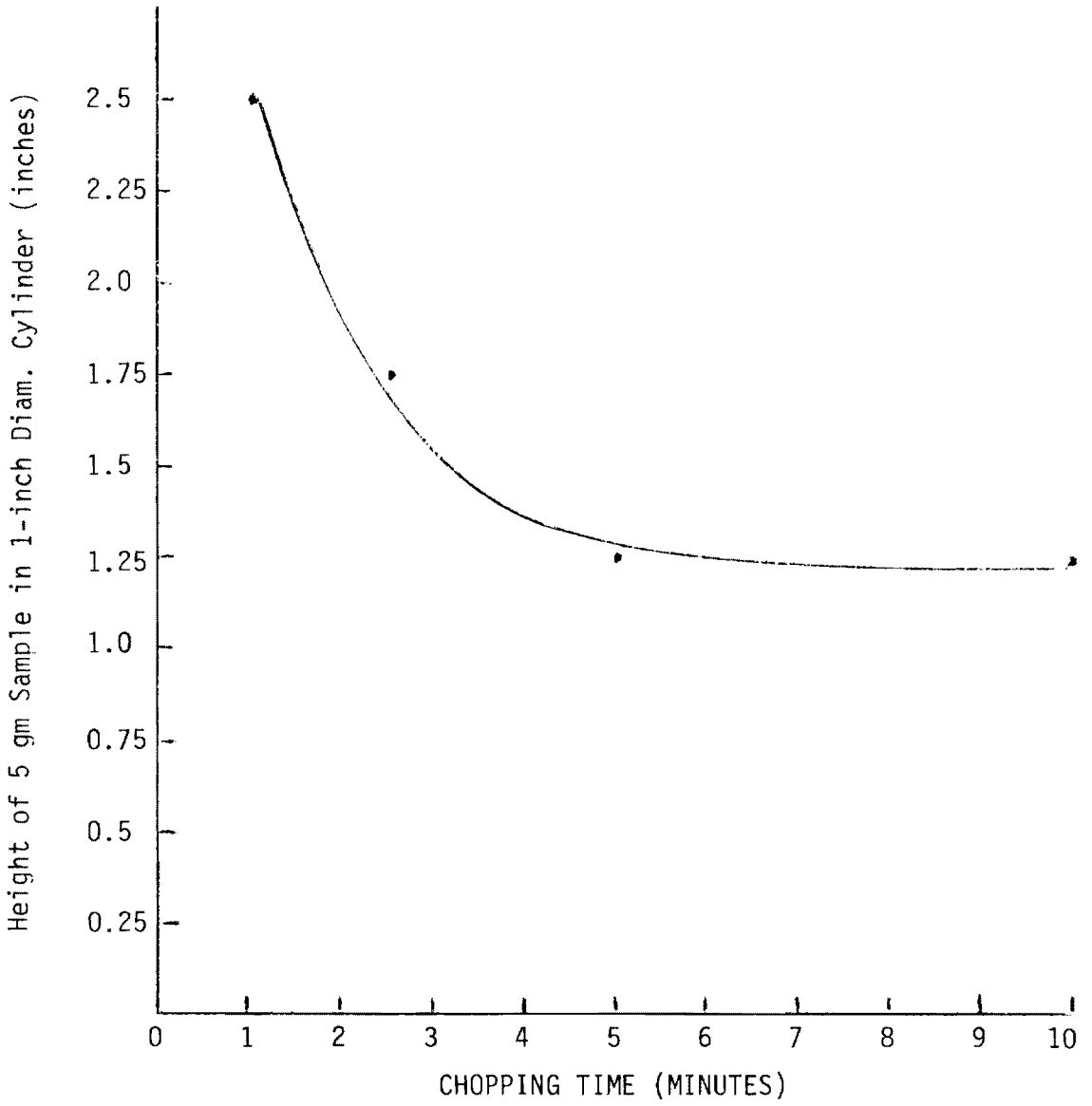


Figure 7. Effect of Chopping Time on Packing Height of Chopped Nextel Fibers.

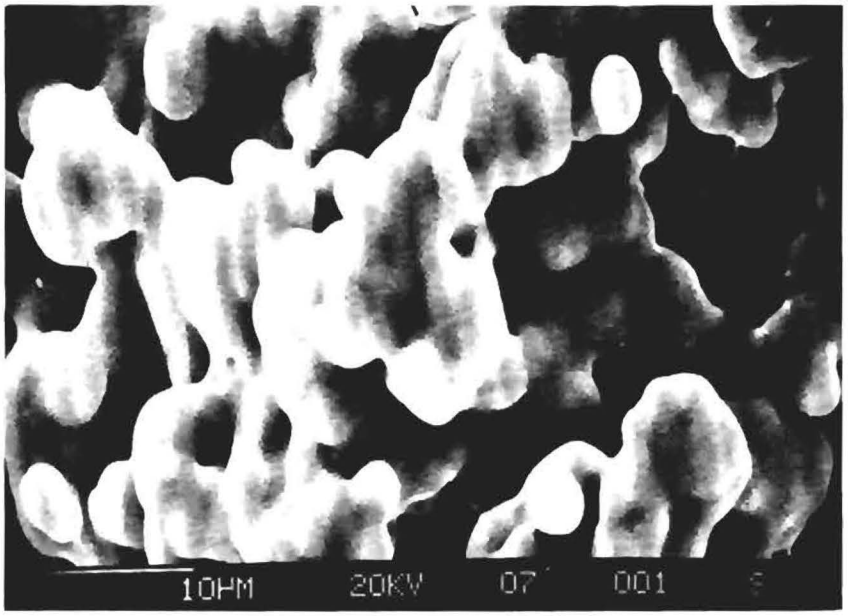


Figure 10. Fine Powder Plus Resin After Firing.

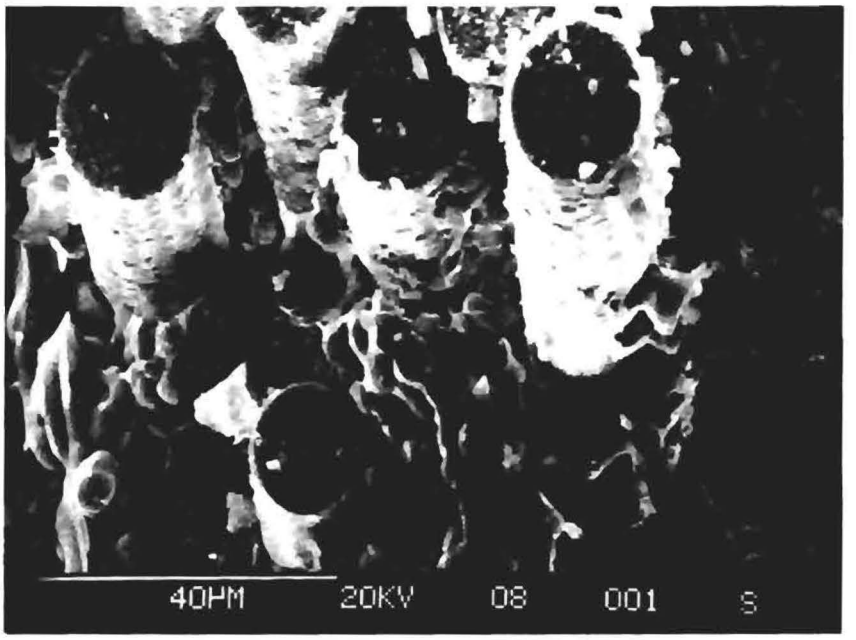
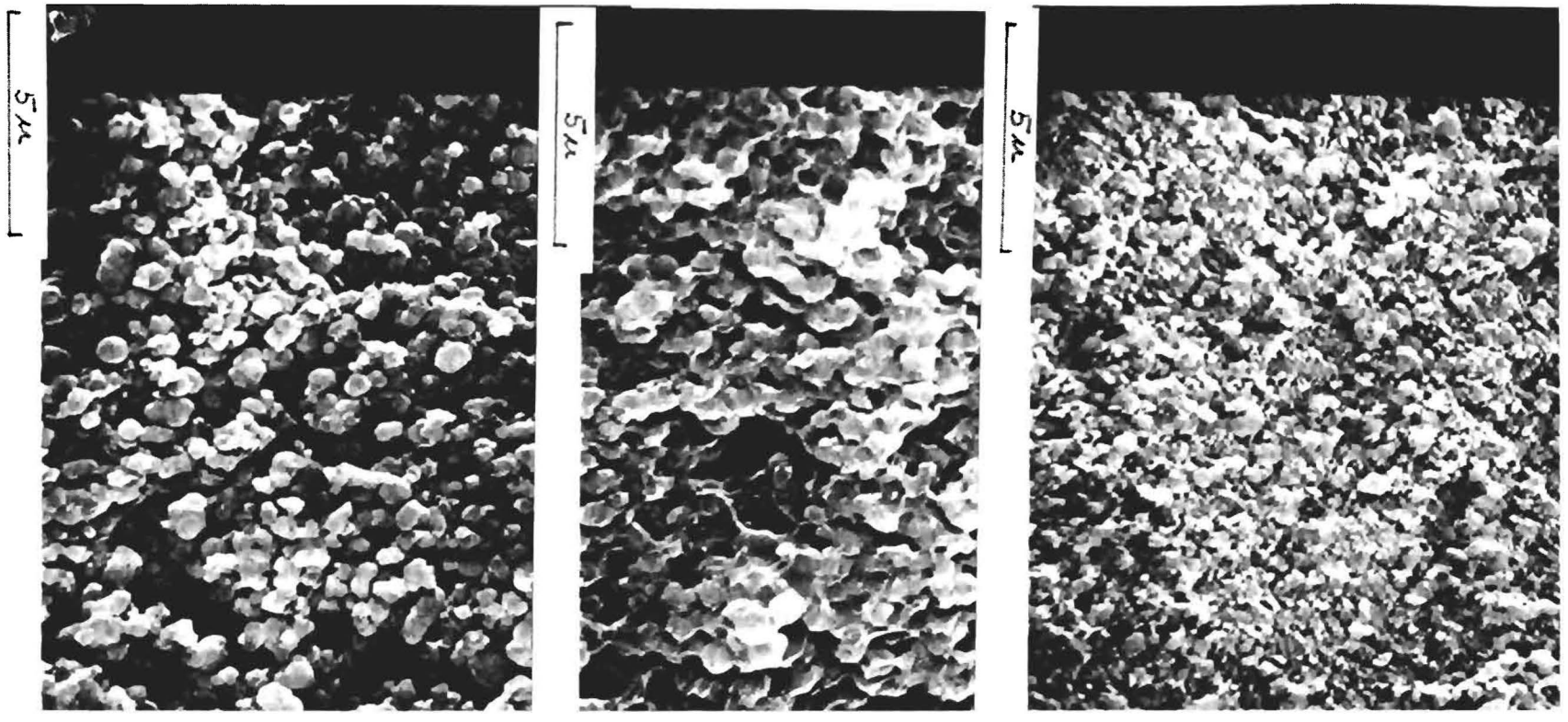


Figure 11. Fine Powder Plus Resin Containing FP Fibers After Firing.

much more of the matrix material adhered to the fiber after firing. In a separate experiment we studied the effect on the green and fired density of the resin/powder mix by varying the amount of SiO_2 derived from the resin when the mixture was pressed at 140 MPa. Figure 12, a, b, and c show the microstructure of compacts containing 38, 29, and 23 percent SiO_2 from the resin in the as-pressed condition. Figure 13, a, b, and c show the same compositions when calcined at 450° C and Figure 14, a, b, and c after firing. Figures 12 and 14 when compared with Figures 8 and 10 illustrate the improvement in green and fired density that is possible through the application of pressure.

Figures 15 and 16 show the microstructure of the coarse powder and resin alone and containing FP fibers before firing. Figures 17 and 18 are after firing. Again matrix penetration was observed between individual fibers although the fiber spacing was of the order of one to two or three fiber diameters. The coarse powder/resin composition appeared to sinter to a higher density than the fine powder/resin composition. Referring to the composite, there appeared to be less fiber/matrix contact and there was essentially no matrix material adhering to the fibers. Again, fiber pull-out was evident in both the fired and unfired composites.

Figures 19 and 20 show the microstructure of the matrix containing fine powder, coarse powder and resin before firing. Figure 21 shows this matrix and resin containing FP fibers before firing. Figures 22 and 23 show the matrix after firing, and Figure 24 shows the matrix with fiber after firing. Figures 19 and 20 suggest that the coarse powder is coated with the fine powder and that the fine powder occupies some portion of the space betwen the coarse particles. As a result of the void space the fired

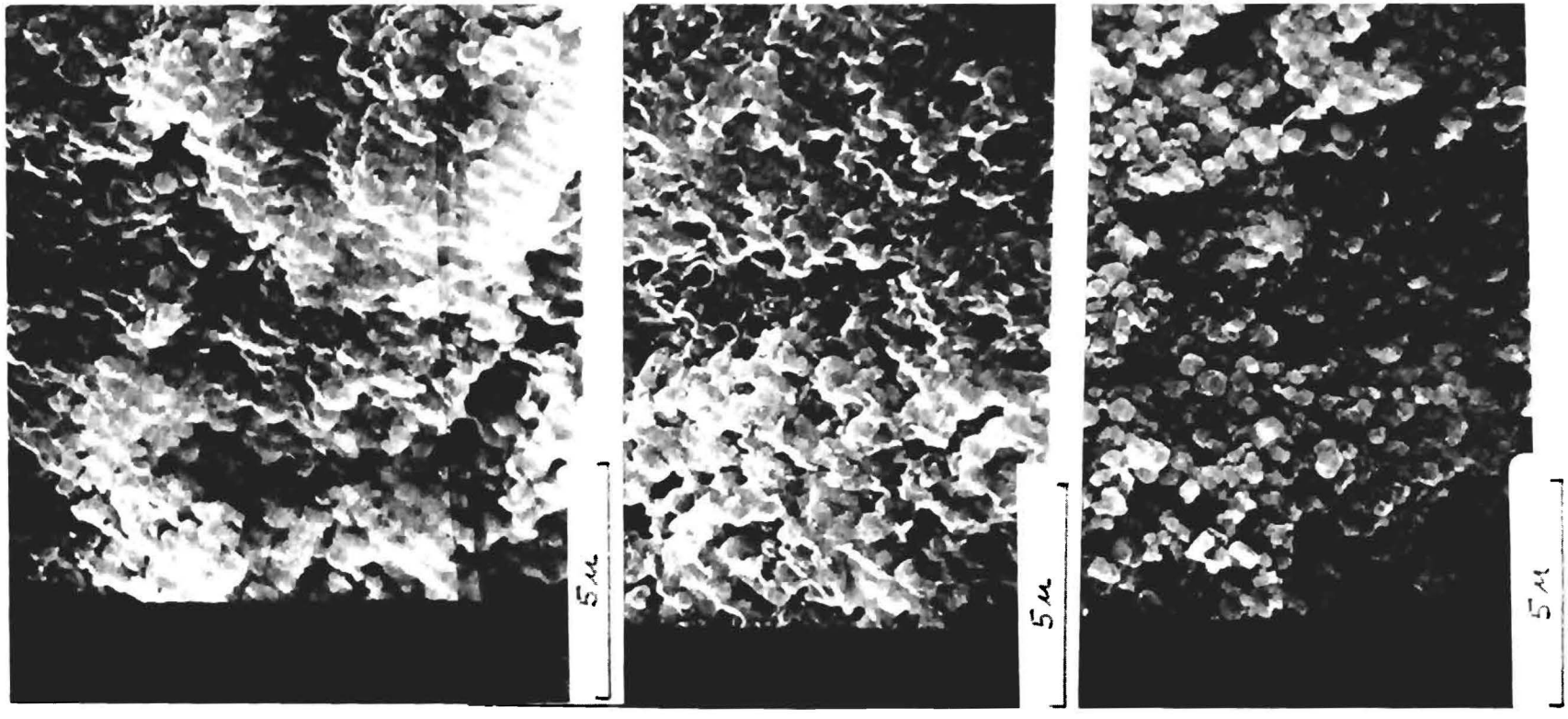


a. 38% SiO_2 from resin

b. 29% SiO_2 from resin

c. 23% SiO_2 from resin

Figure 12. Fine Silica Powder Plus Silica Resin Pressed at 140 MPa - Unfired.

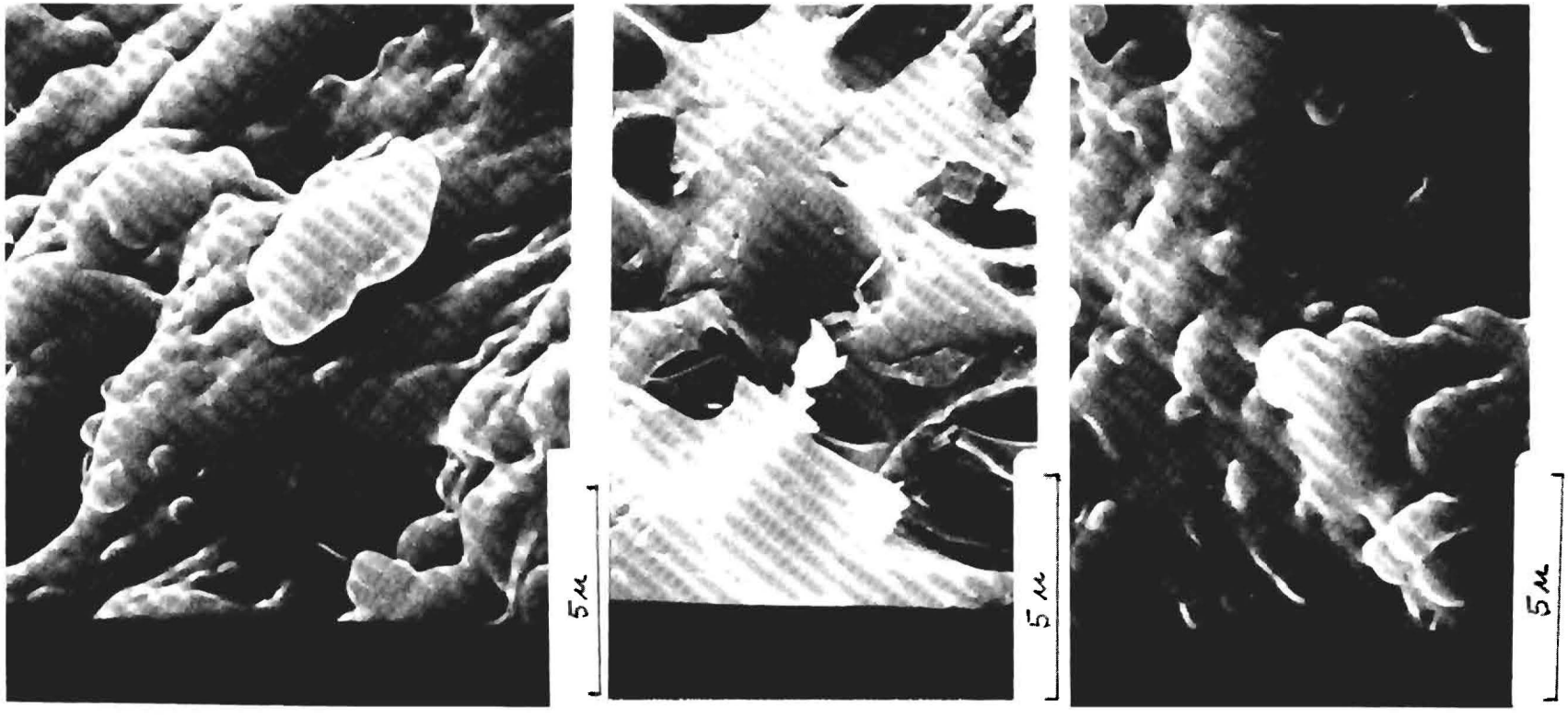


a. 38% SiO_2 from resin

b. 29% SiO_2 from resin

c. 23% SiO_2 from resin

Figure 13. Fine Silica Powder Plus Resin Pressed at 140 MPa and Calcined at 450° C.



a. 38% SiO_2 from resin

b. 29% SiO_2 from resin

c. 23% SiO_2 from resin

Figure 14. Fine Silica Powder Plus Resin Pressed at 140 MPa and Fired at 1315^{o} C for 8 Hours in Vacuum.

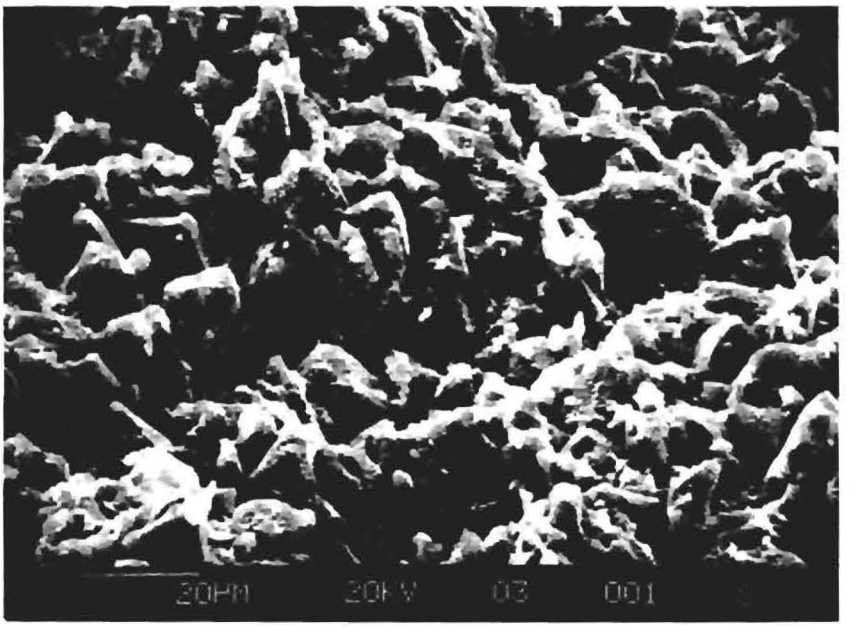


Figure 15. Coarse Powder Plus Resin Before Firing.

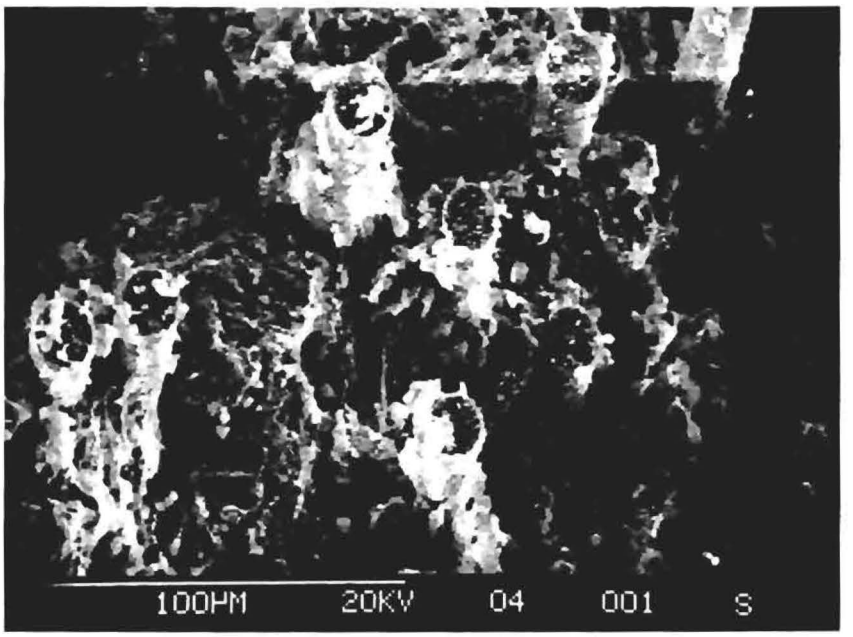


Figure 16. Coarse Powder Plus Resin Containing Fibers Before Firing.

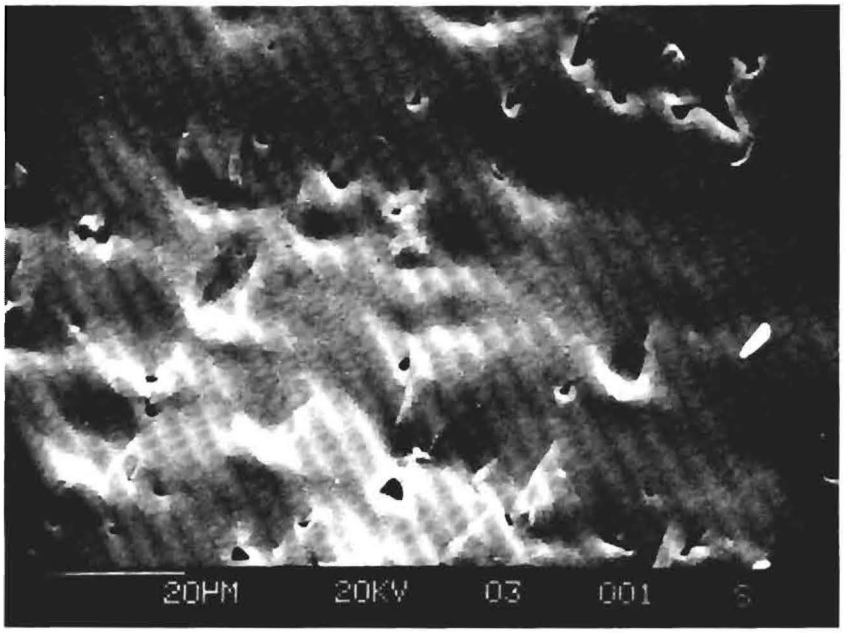


Figure 17. Coarse Powder Plus Resin After Firing.

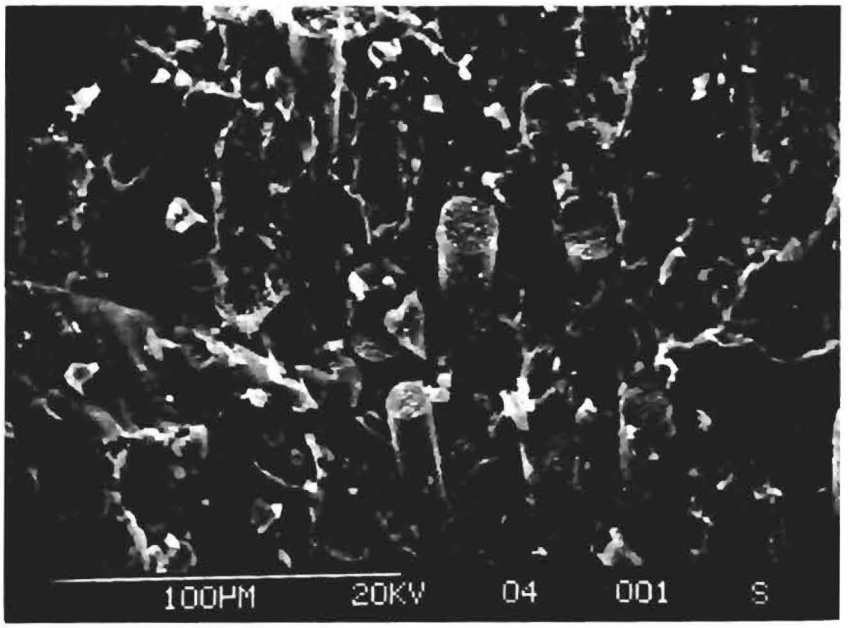


Figure 18. Coarse Powder Plus Resin Containing Fibers After Firing.

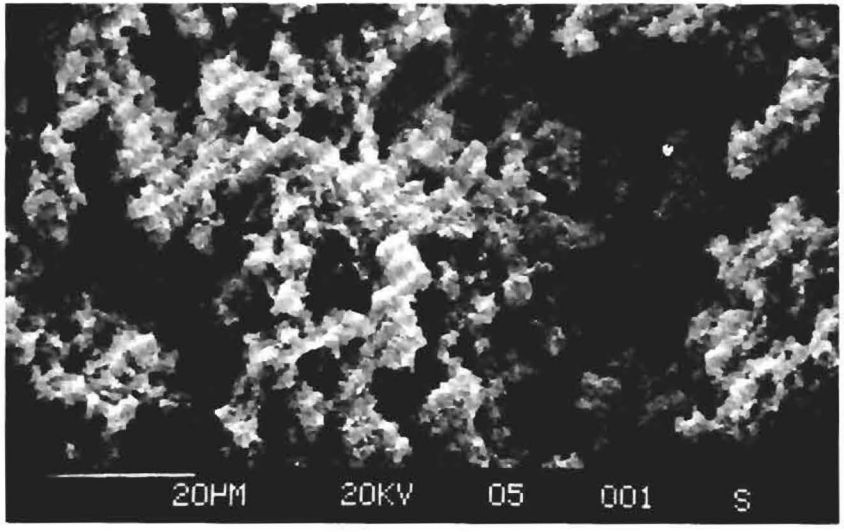


Figure 19. Fine Powder, Coarse Powder, Plus Resin Before Firing.

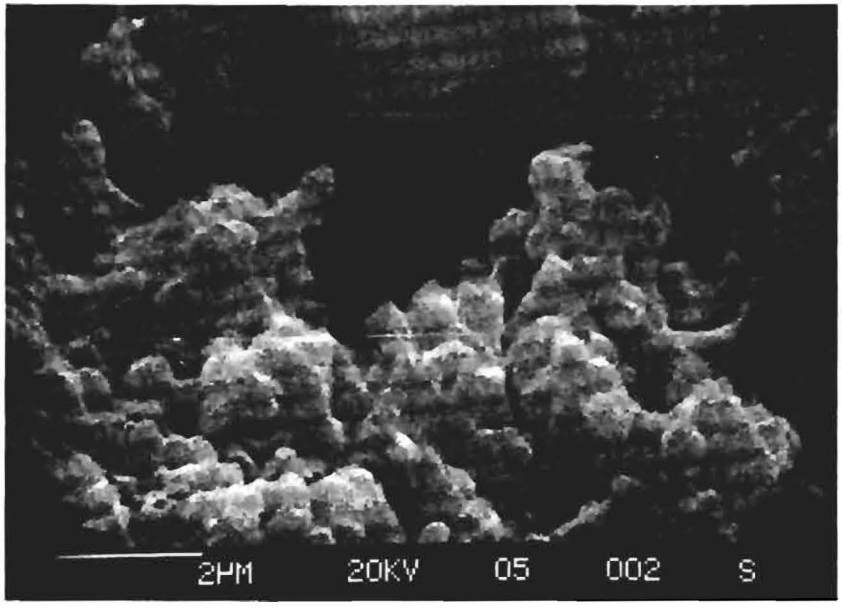


Figure 20. Fine Powder, Coarse Powder, Plus Resin Before Firing.

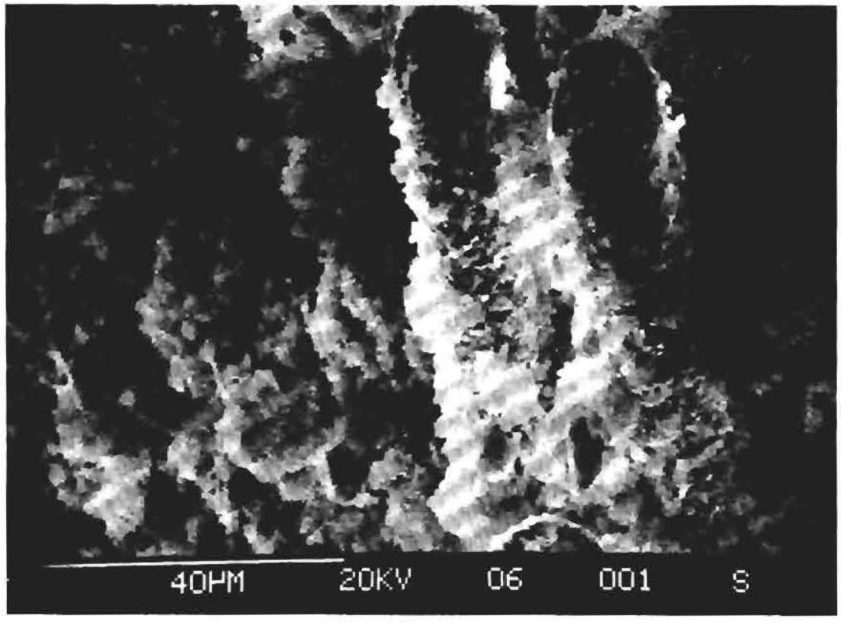


Figure 21. Fine Powder, Coarse Powder, Plus Resin Containing FP Fiber Before Firing.

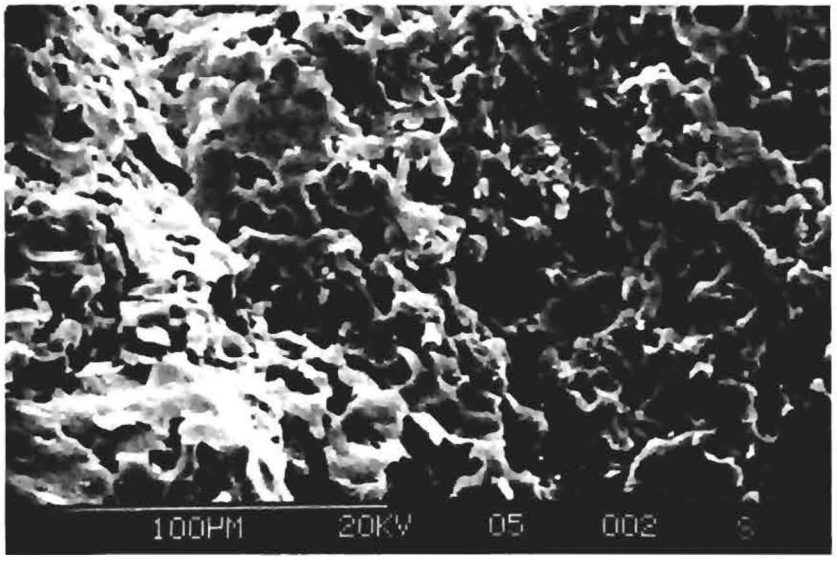


Figure 22. Coarse Powder, Fine Powder, Plus Resin After Firing.

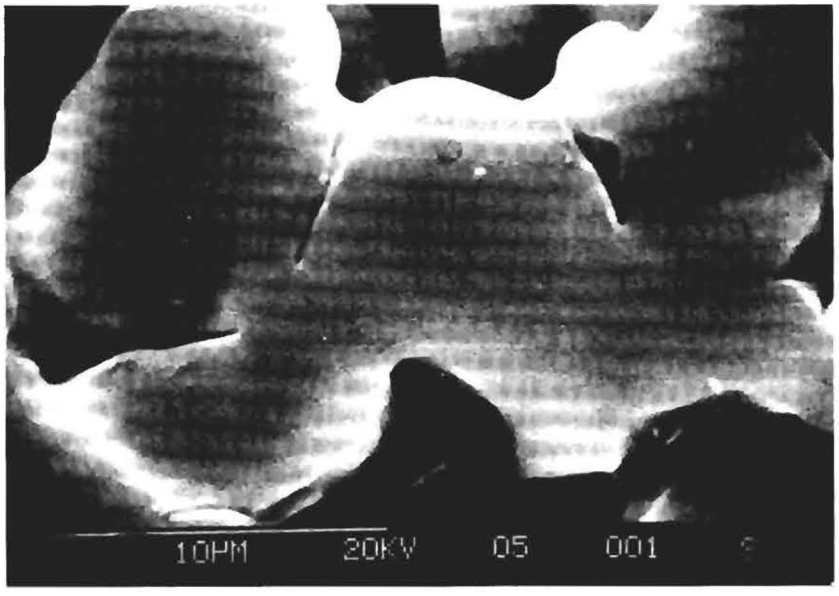


Figure 23. Coarse Powder, Fine Powder, Plus Resin After Firing.

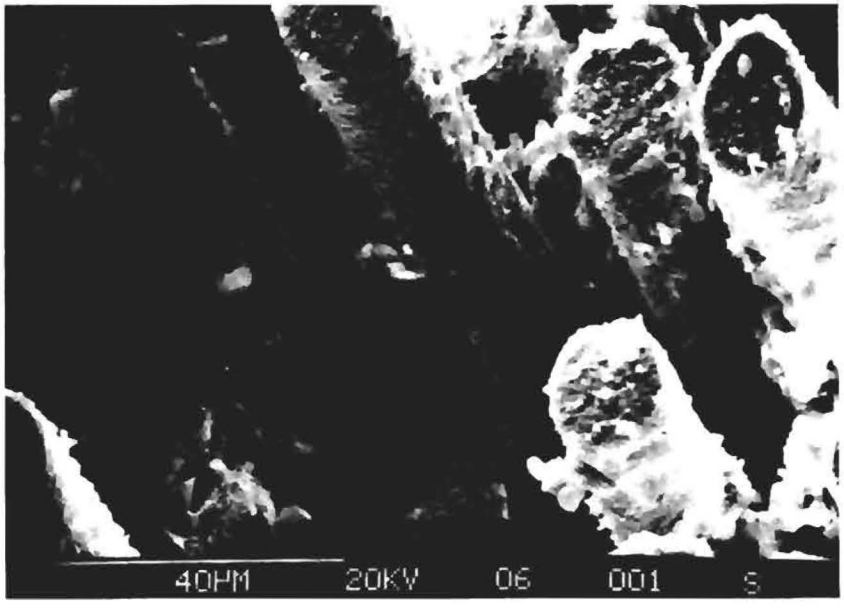


Figure 24. Coarse Powder, Fine Powder Plus Resin Containing FP Fiber After Firing.

matrix shows excessive porosity (Figures 22 and 23). From this experiment it appears that the fine powder may have interfered with the packing and sintering of the coarse powder exhibited in Figures 15 and 17. The three component matrix containing FP fibers shows matrix material adhering to the fibers in both the unfired and fired condition (Figures 21 and 24).

From this preliminary study we observed that matrix sintering appeared to proceed in a similar manner with or without the incorporation of fibers. Fiber pull-out was observed in all cases and fiber spacing was of the order of 1/2 to two fiber diameters. In all cases the matrix easily penetrated the yarn and spaces between individual fibers. Devitrification was not evident in any of the composites containing FP fibers.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. We have produced high purity silica materials as resin, fine powder (0.5 - 1.0 μm) and coarse powder (1 - 40 μm).
2. Eliminated cristobalite formation through the use of ultra high purity materials and vacuum sintering.
3. Developed materials and processing techniques with the potential for producing high green density.
4. Identified candidate fibers and explored interaction and packing with matrix powders and resins.

Recommendations

1. Confirm optimum matrix formulations and processing methods for producing high green densities.
2. Explore and identify critical factors in production of high purity materials with maximum resistance to devitrification.
3. Optimize sintering cycles and atmosphere for producing maximum fired densities consistent with minimum cristobalite formation.
4. Develop isostatic pressing techniques for uniaxial and biaxial composites.
5. Develop slip casting and electrophoresis techniques for composite formations.

REFERENCES

1. J. C. Blome, D. N. Drennan and R. S. Schmitt, "High Purity Silica Reflective Heat Shield Development," NASA CR 137617 MDC D1139 McDonnell Douglas Astronautics Co.-East, October 1974.

2. B. E. Yoldas, "Monolithic Glass Formation by Chemical Polymerization," Journal of Materials Science, 14 (1979) 1843-1849.

3. E. M. Rabinovich, D. W. Johnson, Jr., J. D. MacChesney, E. M. Vogel, "Preparation of Transparent High-Silica Glass Articles from Colloidal Gels," Bell Laboratories, Murray Hill, N. J., (no date).

4. N. G. Ainslie, C. R. Morelock and D. Turnbull, "Devitrification Kinetics of Fused Silica," Symposium on Nucleation and Crystallization in Glasses and Melts, edited by Reser, Smith and Insley, American Ceramic Society, Inc. (1962), pp. 97-107.

5. F. E. Wagstaff and K. J. Richards, "Kinetics of Crystallization of Stoichiometric SiO_2 Glass in H_2O Atmospheres," Journal of American Ceramic Society, Vol. 49, No. 3., 1966, pp 118-121.

6. J. F. Bacon and R. D. Veltri, "Development of Radome Material," AFML-TR-78-97, United Technologies Research Center, Final Report, July 1978.

7. F. Meyer, "Effects of Various Fiber Additions to the Properties of Slip-Cast Fused Silica," Proceedings of the Fifteenth Symposium on Electromagnetic Windows, edited by H. L. Bassett and G. K. Huddleston, June 18-20, 1980, pp 170-178.

8. W. J. Corbett, A. T. Sales and J. D. Walton, Jr., "Improving the Mechanical Properties of Slip-Cast Fused Silica by Fibrous Reinforcement," Georgia Tech Final Report, Project A-793, Contract No. 16-2092 for Sandia Corporation, August 6, 1965.

9. NMAB-376, "High Temperature Metal and Ceramic Matrix Composites for Oxidizing Atmosphere Applications," National Materials Advisory Board, 1981, p 125.

10. Ibid, pp 136.

11. "Cab-O-Sil Properties and Functions," Technical Bulletin, Cabot Corporation, Boston, MA.

12. B. E. Yoldas and D. P. Partlow, "Formation of Monolithic Oxide Materials by Chemical Polymerization," Westinghouse R&D Center, Final Report (ARO Contract DAAG 29-80-C-0055) January 1982.

13. W. Stober, A. Fink and E. Bohn, "Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range," J. of Colloid and Interface Science, Vol. 26, 1968, pp 62-69.

APPENDIX A

CONSTRUCTION OF A 1500° C TUBE FURNACE

A small tube furnace capable of being heated to 1500° C in air was constructed using a modified version of a small laboratory furnace described by Quinn 1/.

The furnace was constructed using readily available materials. The frame is formed using bolt together Slotted Angle®, 2-1/4 x 1-1/2 x 14 gauge, Equipto's number 5600. The top, bottom and sides were formed from Johns-Manville Transite®, a 1/4 inch thick fiber reinforced refractory cement board. The furnace cavity was formed from insulating firebricks (IFB). The bricks were Babcock and Wilcox K-30's. Additional insulation over the top of the cavity was provided using a Harbison-Walker 3 inch thick, 30 lb/ft^3 density fused silica foam and Babcock and Wilcox Kaowool®, an alumino silicate, one inch thick fiber blanket of approximately 8 lb/ft^3 density.

The tube used to provide a controlled atmosphere environment for the sintering studies was 99.8 percent impervious aluminum oxide from the McDanel Refractory Company. The tube was 2 inches in outside diameter with a 1/8 inch wall and was 24 inches in length. The silicon carbide resistance heating elements were 1/2 inch in diameter by 16 inches long and have a 5 inch active heating length. Four elements were used and wired in series. Power was supplied by a 30 amp variable auto-transformer.

The shell of the furnace was formed by bolting the slotted angle together to produce a frame 14-1/2 x 14-1/2 x 15-3/4 inches high. The Transite bottom and four sides were placed in position and a layer of IFB straights (2-1/2 inch wide) placed on the Transite as shown in Figure 1. A second layer of IFB splits (1-1/4 inch thick) was placed in the same

pattern. The third layer was laid up with four IFB straights on edge (2-1/2 inches wide) and four additional straights cut to a width of 2 inches as shown in Figure 2. This formed a cubical cavity 4-1/2 inches on each side. Holes were drilled through two opposite IFB's and through the two transite sides in the pattern shown in Figure 3 to accommodate the four silicon carbide resistance heating elements and the two inch diameter aluminum tube.

The fourth layer of IFB was placed over the cavity arranged in the pattern shown in Figure 1. This layer was covered with a 3 inch thick, 30 lb/ft^3 density fused silica foam block. The fused silica foam block was covered with a one inch thick Kaowool® blanket and the 1/4 inch Transite top bolted in place. A sectional view of the furnace is shown in Figure 4.

The furnace was operated by slowly increasing the voltage on the auto transformer until the desired temperature range was reached. The furnace was operated so as to not exceed a 300^{o} C per hour rate of temperature increase or decrease, which was determined by the heating rate specified for the aluminum oxide tube.

1/ Quinn, G. D., "Guide to the Construction of a Simple 1500^{o} C Test Furnace," AMMRC TR83-1, January 1983 (previously published as AMMRC TN 77-4, August 1977).

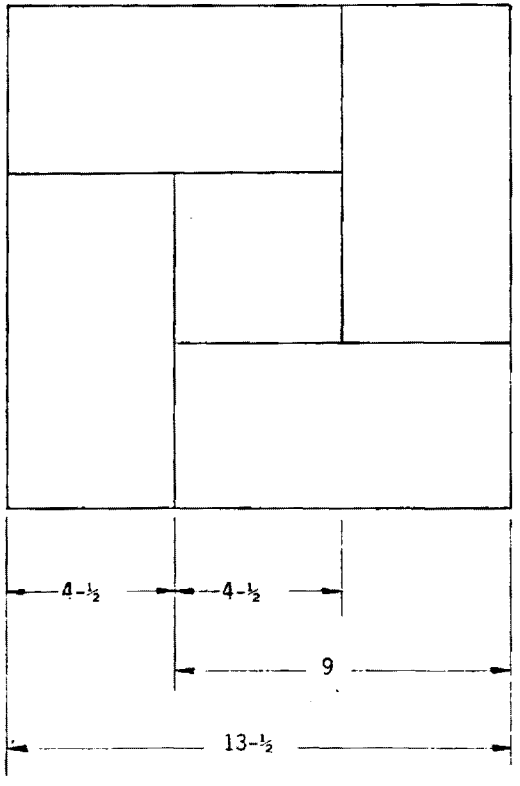


Figure 1. IFB Pattern for First, Second and Fourth Layers

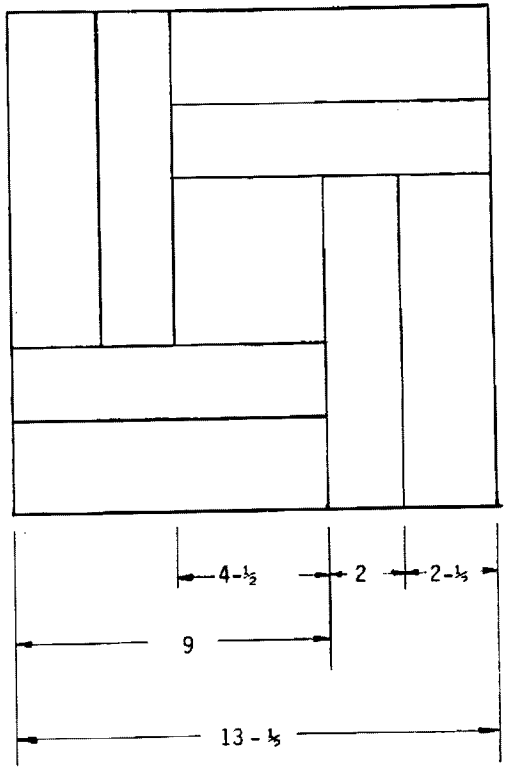


Figure 2. IFB Pattern for Third Layer (Bricks on Edge)

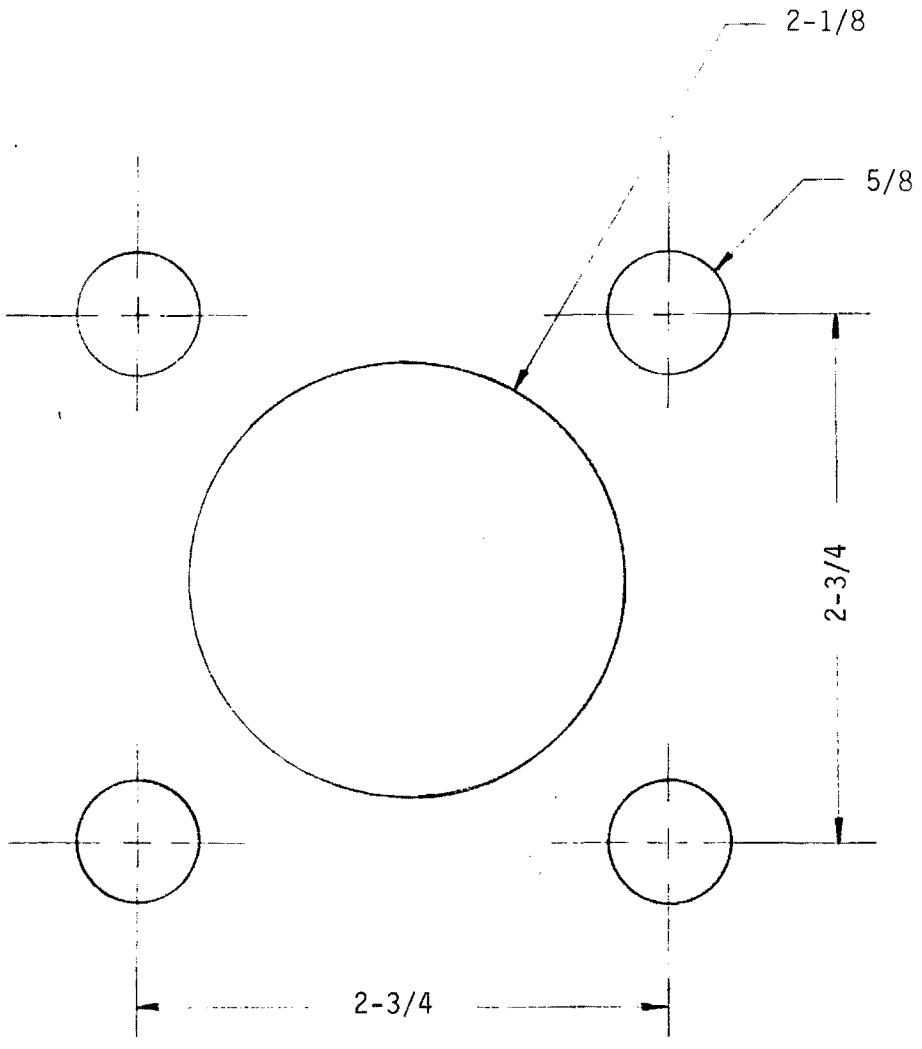


Figure 3. Placement of Heating Elements.

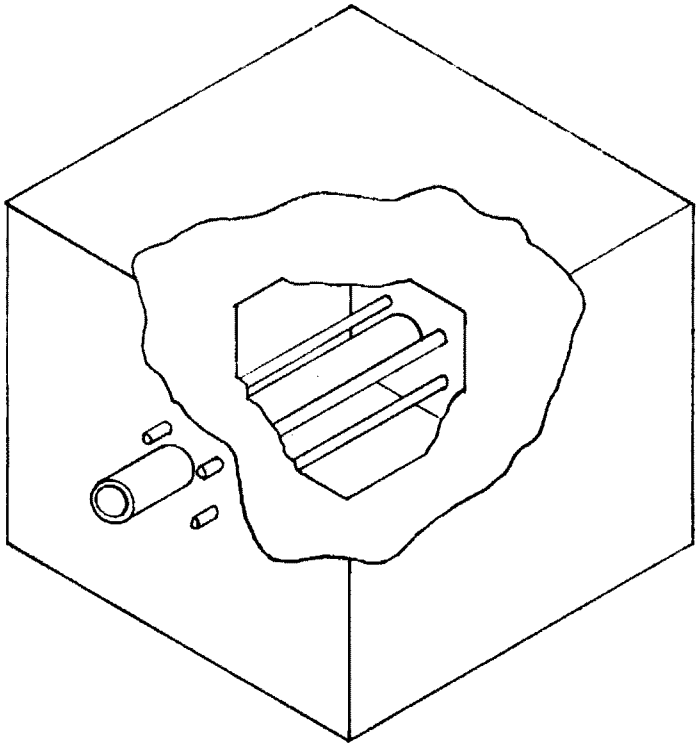


Figure 4. Sectional View.